Selective Interface Control of Order Parameters in Complex Oxides

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Abstract

In complex materials observed electronic phases and transitions between them often involves coupling between many degrees of freedom whose entanglement convolutes understanding of the instigating mechanism. Metal-insulator transitions are one such problem where coupling to the structural, orbital, charge, and magnetic order parameters frequently obscures the underlying physics. Here, we demonstrate a way to unravel this conundrum by heterostructuring a prototypical multi-ordered complex oxide $NdNiO_3$ in ultra thin geometry, which preserves the metal-to-insulator transition and bulk-like magnetic order parameter, but entirely suppresses the symmetry lowering and charge order parameter. These findings illustrate the utility of heterointerfaces as a powerful method for removing competing order parameters to gain greater insight into the nature of the transition, here revealing that the magnetic order generates the transition independently, leading to a purely electronic Mott metal-insulator transition.

Introduction

One of the greatest challenges of condensed matter physics involves exposing the true underlying mechanisms giving rise to the observed anomalous properties, a situation greatly com-

plicated by the coupling of various interactions, for example competing nematic, structural and spin transitions in iron pnictide[1, 2] or intertwined charge, magnetic and superconducting order parameters in underdoped high-Tc cuprates[3, 4]. In strongly correlated electronic materials, the notion of complexity has been synonymous with multiple and often antagonistic ordered phases of intertwined charge, spin, and orbital degrees of freedom[3–7]. True insight into the ground state of these materials thus necessitates the ability to selectively eliminate these degrees of freedom to reveal individual contributions.

As a classic case in question, the crossover of an electrically conducting state of a solid into a phase wherein the movement of carriers is prohibited is a prototypical example of such problem. This metal-to-insulator transition (MIT) is frequently accompanied by emergent order parameters including structural modulation, magnetic, charge, and orbital orderings etc., making it an arduous task to decipher the decisive interaction behind the transition[8]. Despite these complications, metal-insulator transitions have been controllably modified by external stimuli in an effort to disentangle the coupled order parameters to the true progenitor[9–16]. Congruent to this effort, a deterministic control over the interfaces between layers with distinct or competing order parameters has further widened the traditional modalities that govern the global phase behavior of correlated electrons[17–22]. The heterointerface approach naturally brings forward the important question of whether it is possible to selectively modulate a specific ordering to reveal the primary cause for the phase transition into a multi-ordered ground state. Unlike the previously mentioned efforts, where the system comes back to the original ground state when the external stimulus is removed, the present study undertook to suppress order parameters by the virtue of epitaxial stabilization, effectively freezing the system in an atypical state.

Specifically, a 15 unit cell thin film of rare-earth nickelate $NdNiO_3$ (NNO) is utilized as a model system exhibiting a first-order MIT that in the bulk involves structural, charge, and antiferromagnetic order parameters whose entanglement has obscured true understanding of the

mechanism underpinning the transition, Fig. 1A and B[6, 7, 23–39]. Interestingly, recent work by Hepting and Wu *et al* has shown that superlattices utilizing $PrNiO_3$ and $PrAlO_3$ can supress the MI- and CO transitions, while preserving the AFM transition, leading to a rare metallic AFM state[29, 30]. Our experiment, spanning x-ray absorption spectroscopy (XAS) and resonant x-ray scattering (RXS), demonstrates that in the ultra thin limit for films the MIT persists with the same bulk-like E'- antiferromagnetic ordering and changes in electronic structure while the charge order parameter, and accompanying structural transition, are completely removed at all temperatures. These findings imply the exceptional case of an isosymmetric and purely electronic Mott transition[15, 40] driven by strongly correlated electron moments and is in sharp contrast to the present understanding of physics of rare-earth nickelates[35–38].

Electronic and magnetic configuration

Reduction of the degrees of freedom through heterostructuring presumably alters the electronic structure from it's bulk-like state. Indeed, in nickelates, thin-film geometry and proximity to the interface has been shown to strongly alter the electronic structure of the constituent layers and, thus, requires investigation; numerous XAS reports detail the change of the electronic structure across the MIT showing a characteristic splitting of the Ni L_3 edge below the MIT into two distinct peaks and a narrowing of the d-electron bandwidth in the insulating state[6, 7, 25, 33, 41, 42]. These two distinct effects are the spectroscopic signatures of the stabilization of an insulating state in the nickelates. As seen in Fig. 2A, in the case of ultra thin films of NNO, the Ni L_3 edge does indeed show a clear splitting below the MIT. Tracking the intensity in between the two peaks (inset of Fig. 2A) confirms a distinct spectroscopic change quantitatively very close to bulk-like behavior across the MIT[42]. Similarly, the O K-edge pre-peak reflects the band narrowing across the MIT, Fig. 2B; the sudden shift in bandwidth is commensurate with the first-order MIT at $\sim$ 150K, (Fig. 3B, solid lines)[25]. Thus, both

XAS and transport measurements affirm that the ultra thin structural motif does not generate any anomalous electronic structure effects across the MIT, making it an ideal candidate for investigation of the commensurate order parameters.

Spin ordering is a prevalent ingredient in Mott transitions[8, 43]. In the nickelates, the magnetic ordering has received a widespread attention due to the unusual stacking of ferromagnetic planes along the $(1\ 1\ 1)_{pc}$ (pc = pseudo-cubic) direction that are coupled antiferromagnetically (AFM) to one another in an up-up-down-down pattern, a non-collinear periodic behavior and a magnetic unit cell consisting of four structural unit cells, shown in Fig. 1C[44, 45]. Probing this anomalous, E'- AFM ordering in ultra-thin film geometry is quite challenging; Fig. 3A displays the results of the soft x-ray resonant scattering (RXS) at the $(1/2\ 0\ 1/2)_{or}$ (or = orthorhombic) reflection with the energy tuned to the Ni L_3 edge (852 eV) below the MIT. This structurally forbidden Bragg reflection corresponds to a 4-fold unit cell repetition in the $(1\ 1\ 1)_{pc}$ direction. As seen in Fig. 3B, circles, the intensity of this reflection tracks very close with the MIT, suddenly rising above the background noise at around 140K and steadily increasing until beginning to stabilize at low temperature. Both the periodicity and spectroscopic signature are in excellent agreement with previous studies on thick $NdNiO_3$ films and bulk powders[44, 46]. In short, these results show that the bulk E′-type AFM order parameter is preserved and conforms with the MIT despite bi-axial strain ($\sim 1.4\ \%$). With the expected electronic structure response (i.e. AFM order parameter, and first-order MIT) the pinning of the lattice to the substrate does not cause any anomalous perturbation to the bulk-like magnetic and transport behavior of the nickelate film. In addition, for any bulk rare-earth nickelate, the ground state is characterised by the presence of charge ordering (CO) *and* the structural transition from the orthorhombic $Pbnm$ symmetry of the metallic phase to monoclinic $P2_1/n$ symmetry of the insulating phase [6, 7, 36].

Probing lattice symmetry and charge ordering

First, we discuss the issue of lattice symmetry transformation, which is considered to be critical for the MIT. Heterostructuring naturally leads to a modulation of the film lattice due to the strong bonding with the substrate's ions. When the film becomes thick enough the relaxation of elastic strain is inevitable and effectively decouples the film from the substrate[47]. In the ultra thin regime, however, the film is pinned to the substrate with no detectable relaxation and the heteroepitaxy infact controls the lattice degrees of freedom therein[33, 41].

$Pbnm$ (metal) and $P2_1/n$ (insulator) space groups share the same Ni arrangement, however they are split into different Wycoff positions with the symmetry lowering. These inequivalent Ni sites carry a rock-salt pattern of charge disproportionation $Ni^{3\pm\delta}$ giving rise to the CO parameter. In recent years it has been found that, while hard RXS is a powerful tool for investigating charge ordering, careful analysis is required to avoid the misinterpretation of CO for small distortions of the oxygen octahedral network [35, 36, 48]. With this caution in mind, we investigated the $(0\ 1\ 5)_{or}$ and $(1\ 0\ 5)_{or}$ reflections, which are conventionally used to probe the lowering of the symmetry to monoclinic $P2_1/n$, Fig. 4A and B[35, 36, 48–50].

Fig. 4A displays scans along the L reciprocal space vector (L-scan) at the $(0\ 1\ 5)_{or}$ and $(1\ 0\ 5)_{or}$ peaks. The $(1\ 0\ 5)_{or}$ peak is symmetry allowed for orthorhombic NNO, as a Bragg peak corresponds to the Nd sublattice, thus the film peak with Kiessig fringes is anticipated. As expected, this (105) reflection should have no Ni contribution until the charge ordering breaks the *Pbnm* symmetry in the low temperature insulating phase; the CO then leads to an additional contribution to the peak from Ni causing a sharp change in signal strength, especially when the x-rays are tuned to the resonant Ni K-edge (8.34 keV)[36]. Surprisingly, as the temperature is scanned across the MIT no detectable change in the peak intensity is observed, Fig. 4A inset. This result immediately implies that neither charge ordering nor the associated symmetry break-

ing occurs across the transition. In addition, the $(0\ 1\ 5)_{or}$ peak, which is symmetry forbidden for *Pbnm* , does not appear at any temperature, thus confirming the isosymmetric nature of the MIT.

Furthermore, a key feature of resonant scattering is that the additional terms within the scattering factor are $highly$ sensitive to the x-ray energy around an absorption edge[51, 52]. Fig. 4B shows the energy scan at the $(1\ 0\ 5)_{or}$ peak which further corroborate the above picture with higher sensitivity, confirming that *no Ni resonance signal (i.e. symmetry lowering) is detected below the MIT*. This is in stark contrast to all previous reports on both thick films and bulk where strong, temperature dependent resonance was shown to track with the MIT[35–38]. To further verify this finding, the allowed $(2\ 2\ 0)_{or}$ reflection was measured and shows the expected Ni resonance signal, confirming that the Ni contribution is certainly detectable in our experimental setup. These results confirm that across the MIT (*i*) no bond disproportionation of NiO_6 occurs and the metallic phase *Pbnm* lattice symmetry is preserved [36, 37], and (*ii*) since no detectable Ni resonance is observed no charge ordering occurs emerges in the insulating phase . These findings imply that the ultra thin films have stabilized a previously unknown nickelate ground state consisting of an insulating orthorhombic phase with AFM order. Intriguingly, as observed here, the case of a phase transition without a structural symmetry change can only be first order and is exceptionally rare in complex materials, with the most prominent examples being analogous to the liquid-gas transformation[43, 53]. For complex oxides, there are only two known cases of this type of MIT, i.e. Cr-doped V_2O_3 [15] and the surface driven $Ca_{1.9}Sr_{0.1}RuO_4$[40].

Theoretical Presage

Driven by the heterointerface, CO removal and the stabilization of the unknown Mott phase within this class of materials is of great interest and yet has some precedent in past theoretical work [39, 54–61]. For example, two recent studies utilizing different theoretical methods

by Lee *et al* [54, 55] have proposed that the CO is slaved to the E'-magnetic ordering in the weak coupling limit, and can indeed disappear under certain conditions; in particular, using Landau theory, the theory suggests that restricting the nickelates to the ultra-thin film regime may remove the CO. On the other hand, the predicted phase changes the Q-vector for the anti-ferromagnetic ordering, which is in variance with the experiment. Beyond this , Park *et al* have demonstrated that within dynamical mean field theory (DMFT), despite the near Fermi-energy imbalance in the spectral weight between the two Ni sites, the total valence of Ni on both sites is practically identical, with the two different Ni sites instead hybridizing with O, leading to an S = 1 state on the larger octahedra ($3d^8$) and an S = 0 state formed due to AFM coupling with the O holes ($3d^8\underline{\underline{L}}$)[60, 61]. However, when the lattice symmetry is raised to *Pbnm* a metallic state with no MIT has emerged. More recently, Johnston *et al* [59] utilized Hartee-Fock methods to show the NiO_6 octahedra form a alternating collapsed and expanded octahedra, giving a d^8 + $d^8\underline{L}^2$ state, where no CO on Ni occurs.

Finally, using LSDA + U calculations, Yamamoto *et al* [39] obtained results that are in the good agreement with our observations. Specifically, the calculated electronic and magnetic structure in orthorhombic NNO is found to be an insulating state with no Ni CO (as expected for equivalent Ni sites in $Pbnm$ symmetry). In addition, the calculation shows that magnetic space group is lowered to monoclinic due to different spin density polarizations around two O sites that preserve the equivalence of Ni sites in the *Pbnm* space group. Most importantly, this symmetry breaking state involving holes on oxygen and driven by the Hubbard U, opens an insulating gap, which agree well with the previous work [62]. At this point we can conjecture that while in the bulk structural symmetry is indeed lowered to $P2_1/n$, the epitaxial interface is able to preserve the orthorhombic structural symmetry of the metallic phase. The resulting ground state, observed experimentally, can be obtained within the LSDA + U framework, supporting the notion that the bulk-like MIT and magnetic order parameter can be attained with the charge

and structural order parameters removed. In this work, we find the heterointerface acts as a powerful tool to effectively isolate the magnetic order parameter, which drives the bulk-like MIT independently. Thus, by constraining symmetry solutions via substrate imprinting, it is possible to bound order parameter space allowing inter-order behavior to be studied.

Concluding Remarks

In conclusion, the reduction of the number of simultaneously competing order parameters commensurate with a phase transition from a metallic to a Mott insulating state has been achieved on a prototypical ultra thin film of NNO. The thin film heteroepitaxy prevents symmetry lowering from *Pbnm* to $P2_1/n$ across the MIT, thus removing the bulk-like CO parameter. Despite this anomalous state, the Mott MIT persists with no significant effect on the magnetic order parameter. The magnetic order parameter is identified as the culprit which drives the pure electronic MIT in the nickelates, highlighting the utility of this emerging method to sunder the competing order parameters. Our findings suggest that application of this method to eliminate specific order parameters to highly entangled or "hidden" orders found in cuprates, pnictides, heavy fermions and chalcogenides families may shed new light on their anomalous ground states.

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References and Notes

[1] R. M. Fernandes, A. V. Chubukov, & J. Schmalian, *Nature Physics* **10**, 97 (2014).

[2] David C. Johnston, *Advances in Physics* **59**, 803 (2010).

[3] Subir Sachdev, *Rev. Mod. Phys* **75**, 913 (2003).

[4] N. P. Armitage, P. Fournier, & R. L. Greene, *Rev. Mod. Phys.* **82**, 2421 (2010).

[5] Myron B. Salamon & Marcelo Jaime, *Rev. Mod. Phys.* **73**, 583 (2001).

[6] María Luisa Medarde, *J. Phys.: Condens. Matter* **9**, 1679 (1997).

[7] G. Catalan, *Phase Transitions* **81**, 729 (2008).

[8] M. Imada, A. Fujimori, & Y. Tokura, *Rev. Mod. Phys.* **70**, 4 (1998).

[9] M. M. Qazilbash *et al*, *Science* **318**, 1750 (2007).

[10] Vance R. Morrison *et al*, *Science* **346**, 445 (2013).

[11] L. Stojchevska *et al*, *Science* **344**, 177 (2014).

[12] C. H. Ahn *et al*, *Science* **284**, 1152 (1999).

[13] Jaewoo Jeong *et al*, *Science* **339**, 1402 (2013).

[14] A. T. Bollinger, G. Dubuis, J. Yoon, D. Pavuna, J. Misewich & I. Božović, *Nature* **472**, 458 (2011).

[15] P. Limelette *et al*, *Science* **302**, 5642 (2003).

[16] H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, *Science* **270**, 961 (1995).

[17] Jak Chakhalian, J. W. Freeland, A. J. Millis, C. Panagopoulos, & J. M. Rondinelli, *Rev. Mod. Phys.* **86**, 1189 (2014).

[18] J. Mannhart & D. G. Schlom, *Science* **327**, 1607 (2010).

[19] H. Y. Hwang *et al*, *Nature Materials* **11**, 103 (2012).

[20] J. Chakhalian *et al*, *Science* **318**, 1114 (2007).

[21] J. Chakhalian *et al*, *Nature Physics* **2**, 244 (2006).

[22] J. Chakhalian, A. J. Millis, and J. Rondinelli, *Nat. Mat.* **11**, 92-94 (2012)

[23] J. Chakhalian *et al*, *Phys. Rev. Lett.* **107**, 116805 (2011).

[24] Jian Liu *et al*, *Phys. Rev. Lett.* **109**, 107402 (2012).

[25] Jian Liu *et al*. *Nat. Comm.* **4**, 2714 (2013).

[26] Jian Liu *et al.*, Phys. Rev. B **83**, 161102(R) (2011).

[27] I. I. Mazin *et al*, *Phys. Rev. Lett* **98**, 176406 (2007).

[28] A. Frano *et al*, *Phys. Rev. Lett.* **111**, 106804 (2013).

[29] M. Hepting *et al*, *Phys. Rev. Lett.* **113**, 227206 (2014).

[30] M. Wu *et al*, *Phys. Rev. B* **91**, 195130 (2015).

[31] Hauser *et al*, *Appl. Phys. Lett.* **106**, 092104 (2015).

[32] Eva Benckiser *et al*, *Nature Materials*, **10**, 189 (2011).

[33] Jian Liu, M. Kareev, B. Gray, J. W. Kim, P. Ryan, B. Dabrowski, J. W. Freeland, and J. Chakhalian, *Appl. Phys. Lett.* **96**, 233110 (2010).

[34] Y. Bodenthin, U. Staub, C. Piamonteze, M. García-Fernández, M. J. Martínez-Lope, and J. A. Alonso, J. Phys.: Condens. Matter **23**, 036002 (2011).

[35] U. Staub *et al*, *Phys. Rev. B* **71**, 214421 (2005).

[36] J. E. Lorenzo, J. L. Hodeau, L. Paolasini, S. Lefloch, J. A. Alonso, and G. Demazeau, Phys. Rev. B **71**, 045128 (2005).

[37] V. Scagnoli, U. Staub, M. Janousch, A. M. Mulders, M. Shi, G.I. Meijer, S. Rosenkranz, S. B. Wilkins, L. Paolasini, J. Karpinski, S. M. Kazakov, and S. W. Lovesey, Phys. Rev. B **72**, 155111 (2005).

[38] V. Scagnoli *et al*, *Jour. Mag. Mag. Mat.* **272-276**, 420-421 (2004).

[39] Susumu Yamamoto and Takeo Fujiwara, *J. Phys. Soc. Jpn.* **71**, 1226 - 1229 (2002).

[40] R. G. Moore *et al*, *Science* **318**, 615 (2007).

[41] D. Meyers *et al*, *Phys. Rev. B* **88**, 075116 (2013).

[42] John W. Freeland, Michel van Veenendaal, & Jak Chakhalian, arXiv:1504.02802 (2015).

[43] Daniel I. Khomskii, *Basic aspects of the quantum theory of solids*, (Cambridge University Press, Cambridge, MA 2010).

[44] V. Scagnoli *et al*, *Phys. Rev. B* **73**, 100409(R) (2006).

[45] V. Scagnoli *et al*, *Phys. Rev. B* **77**, 115138 (2008).

[46] J. L. Garcia-Munoz, J. Rodriquez-Carvajal, P. Lacorre, *Phys. Rev. B* **50**, 2 (1994).

[47] Andrei R. Kaul, Oleg Yu Gorbenko, & Anton A. Kamenev, *Russ. Chem. Rev.* **73**, 861 (2004).

[48] J. Garcia, M. C. Sanchez, G. Subias, J. Blasco, *J. Phys.: Condens. Matter* **13**, 3229-3241 (2001).

[49] Distinguishing between these peaks requires single-domain films, which are found for NNO on NGO but not when grown on cubic (e.g. $SrTiO_3$) or tetragonal (e.g. $SrLaAlO_4$) substrates.

[50] M. H. Upton *et al*, arXiv:1412.0676v2 (2014).

[51] J. Fink, E. Schierle, E. Weschke, J. Geck, *Rep. Prog. Phys.* **76**, 056502 (2013).

[52] J.-L. Hodeau *et al*, *Chem. Rev.* **101**,1843-1867 (2001).

[53] Hiroshi Shimahara, *J. Phys. Soc. Jpn.* **74**, 823 (2005).

[54] SungBin Lee, Ru Chen, and Leon Balents, *Phys. Rev. Lett.* **106**, 016495 (2011).

[55] SungBin Lee, Ru Chen, and Leon Balents, *Phys. Rev. B* **84**, 165119 (2011).

[56] Sergey Prosandeev, L. Bellaiche, and Jorge Íñiguez, *Phys. Rev. B* **85**, 214431 (2012).

[57] T. Mizokawa, D. I. Khomskii, and G. A. Sawatzky, *Phys. Rev. B* **61**, 17 (2000).

[58] Bayo Lau and Andrew J. Millis, *Phys. Rev. Lett.* **110**, 126404 (2013).

[59] Steve Johnston *et al.*, *Phys. Rev. Lett.* **112**, 106404 (2014).

[60] Hyowon Park, Andrew J. Millis, and Chris A. Marianetti, *Phys. Rev. Lett.* **109**, 156402 (2012).

[61] Hyowon Park, Andrew J. Millis, and Chris A. Marianetti, *Phys. Rev. B* **89**, 245133 (2014).

[62] M. K. Stewart, Jian Liu, M. Kareev, J, Chakhalian, and D. N Basov, *Phys. Rev. Lett* **107**, 176401 (2011).

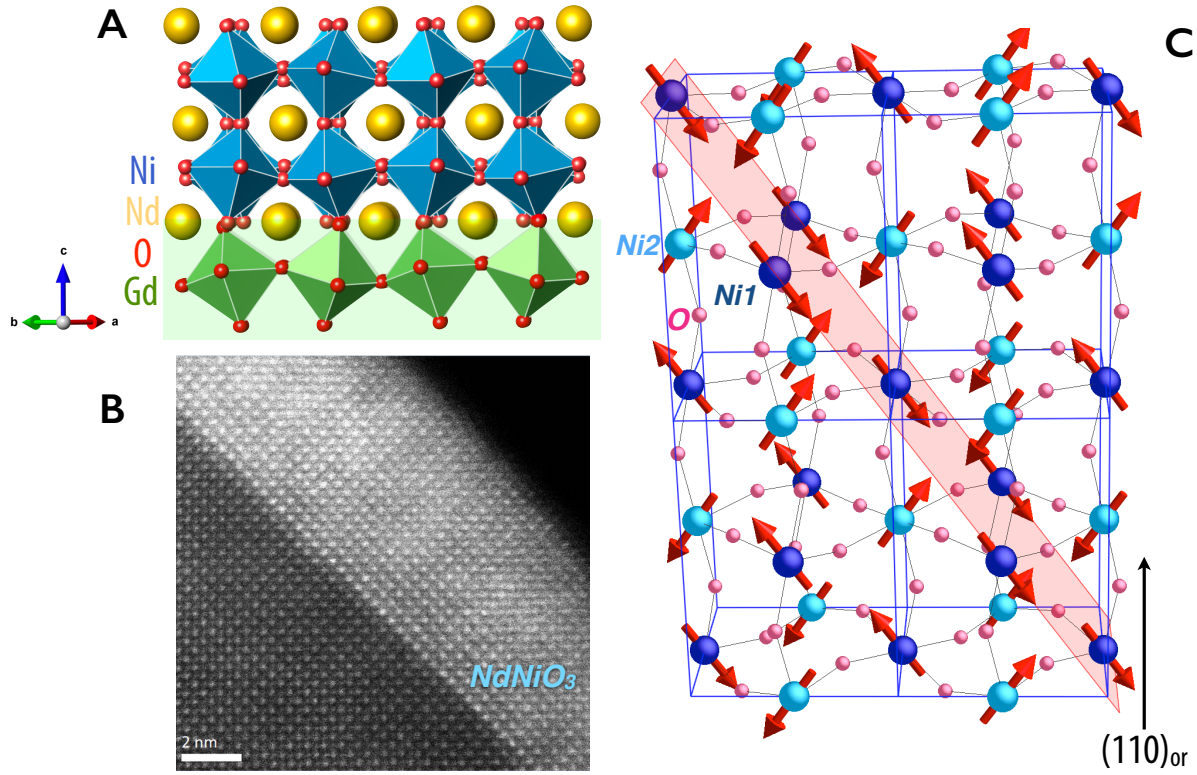

Figure 1: (Color online) (**A**) Heterostructure interface of NNO grown on NGO. (**B**) TEM showing atomically sharp interface. (**C**) E′-type antiferromagnetic ordering in the nickelates with the $(111)_{pc}$ plane highlighted. The dark and light blue spheres represent the nickel sites with charge of $3 \pm \delta$[44, 45].

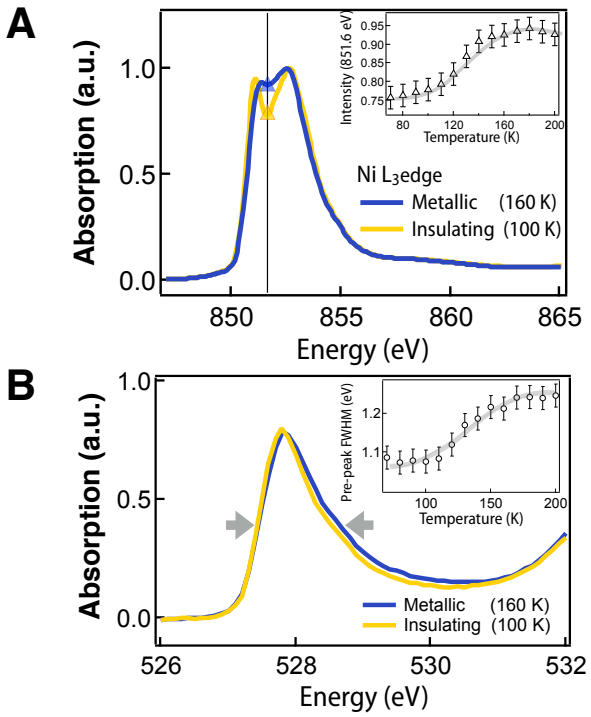

Figure 2: (Color online) (**A**) XAS at the Ni L_3-edge for the metallic and insulating states. Inset shows the intensity between the Ni^{3+} and multiplet peaks, highlighting the sudden narrowing of the peaks across the MIT. (**B**) XAS at the O K-edge for the same. Inset shows the change in the FWHM, arrows, of the O prepeak showing the bandwidth narrowing. All hatched lines are guides to the eye.

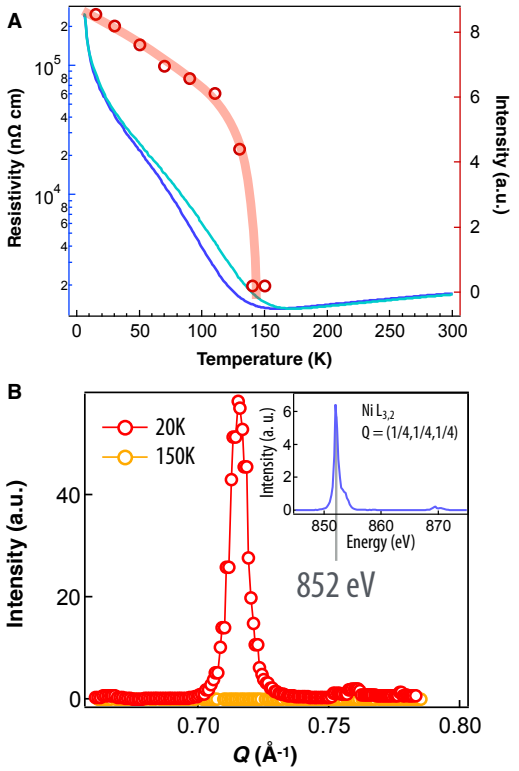

Figure 3: (Color online) (**A**) Left axis: Temperature dependence DC transport for cooling (blue) and warming (cyan) cycles showing a strong hysteresis typical of the first-order MIT. Right Axis: Temperature dependence of the forbidden Bragg peak intensity corresponding to the magnetic order parameter. (**B**) Low and high temperature magnetic Bragg peak corresponding to E′-type anti-ferromagnetism. The inset shows the resonant energy scan at the Ni L_3 and L_2 at the peak.

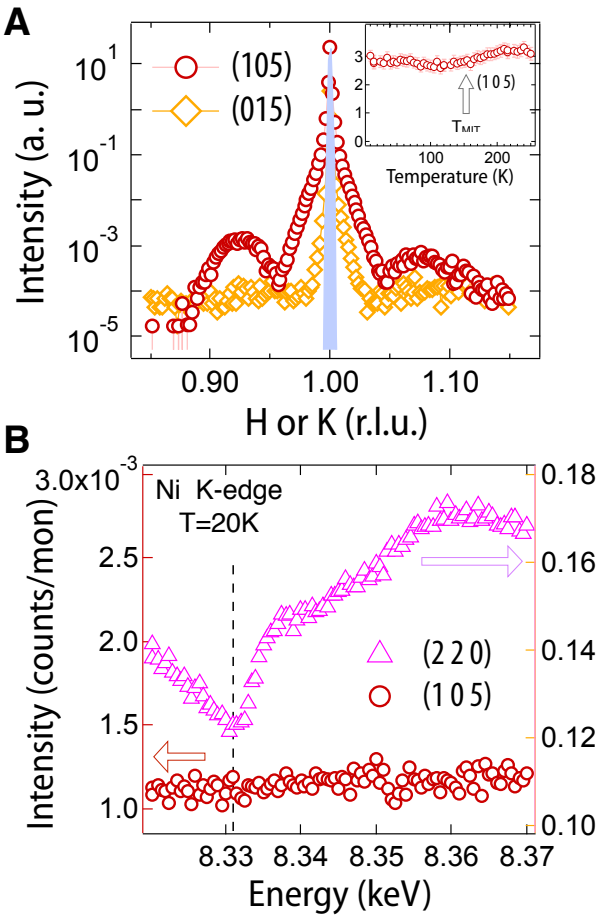

Figure 4: (Color online) (**A**) Scattering around the $(1\ 0\ 5)_{or}$ and $(0\ 1\ 5)_{or}$ peaks at low temperature ~ 10 °K (the sharp peak at 1.00 is the substrate). The inset show the measured intensity of the $(1\ 0\ 5)_{or}$ peak for several temperatures crossing the MIT. (**B**) Ni K-edge resonance scans at the $(1\ 0\ 5)_{or}$ and $(2\ 2\ 0)_{or}$ peaks.